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(54) Surface coated cutting tool

(57) (Object)

The invention relates to a cutting tool whose surface is coated with a composite hard layer formed by means of chemical vapor deposition and having excellent wear resistance and chipping resistance.

(Construction)

A cutting tool consists substantially of a substrate whose surface is coated with a composite hard layer consisting substantially of an inner layer including one or more layers of titanium carbide, titanium nitride, titanium carbonitride, titanium carboxide, and titanium oxycarbonitride, and an outer layer including at least one alumina layer. The alumina layer contains so much *x*-type alumina that an X-ray intensity ratio I_A/I_B of two specific crystal faces A and B in X-ray diffraction is not smaller than 2, where the A-face and B-face denote faces of *x*-type alumina defined as those whose interfacial distances are 2.79Å and 2.57Å in ASTM4-0878, and I_A and I_B denote X-ray intensity of the faces A and B in X-ray diffraction.

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DETAILED DESCRIPTION OF THE INVENTION

[Field of industrial application]

5 The present invention relates to a surface coated cutting tool having excellent wear resistance and chipping resistance, the cutting tool including a cemented carbide substrate whose surface is coated with a composite hard layer formed by means of chemical vapor deposition, the composite hard layer consisting substantially of an inner layer including one or more layers of titanium carbide, titanium nitride, titanium carbonitride, titanium carboxide, and titanium oxycarbonitride (hereinafter referred to generally as titanium
10 compound layers), and an outer layer including at least one alumina layer.

[Prior art]

15 For the purpose of continuous and interrupted cutting of steel, it has been well known practice to use a surface coated cutting tool including a cemented carbide substrate whose surface is coated with a composite hard layer formed by means of chemical vapor deposition, the composite hard layer consisting substantially of an inner layer including a titanium compound layer and an outer layer including at least one alumina layer.

20 The alumina layer is chemically stable and displays excellent face wear resistance, but it adheres poorly to the substrate and lacks toughness. Thus, the surface of the cemented carbide substrate is coated first with a titanium compound layer formed by means of chemical vapor deposition, then an alumina layer is formed on the titanium compound layer by means of chemical vapor deposition, thereby giving wear resistance and toughness to the formed composite hard layer to improve chipping resistance.

25 For the purpose of forming the alumina layer of the composite hard layer by means of chemical vapor deposition, a method is known for speeding up the growth rate of the alumina layer by using a reaction gas obtained by adding 0.01 to 1.0 vol % of hydrogen sulfide gas to the normal reaction gas.

30 The use of this method shortens the time during which the inner layer made of titanium compound and the cemented carbide substrate are held at high temperature, with the result that the structure of the inner layer and the substrate is unlikely to change. Thus, it is said that a surface coated cutting tool having a better performance than the conventional tools can be obtained according to this method (refer to, for example, Japanese Examined Patent Publication 62-3234).

35 The alumina layer obtained by using a reaction gas containing 0.01 to 1.0 vol % of hydrogen sulfide gas is mainly an α -type alumina layer. It is also known that a γ -type alumina layer is obtainable by changing the volume of carbon dioxide gas in the reaction gas.

[Problems to be solved by the invention]

40 In recent years, there has been an increasing demand for a labor-saving and more rapid cutting operation. This demand strongly requires a high speed in continuous and interrupted cutting operation, that is both high speed feeding and high speed cutting under more severe conditions. During the high speed cutting operation, the temperature of the cutting edge rises above 1000°C and steel chips of exceedingly high temperature pass along the face of the cutting tool, which accelerates wear of the face. Thus, the cutting tool is chipped or damaged at a relatively early stage. Under these severe conditions, the cutting tools coated with the composite hard layer including the conventional alumina layer have a relatively short lifetime because the coated layer has insufficient wear resistance and chipping resistance.

[Means for solving the problem]

45 In view of the above, the inventors of the present invention carried out a research to develop a cutting tool whose surface is coated with a composite hard layer including an alumina layer having better wear resistance and chipping resistance than the prior art and obtained the following results.

50 A cutting tool comprising a substrate whose surface is coated with a composite hard layer consisting substantially of an inner layer including one or more layers of titanium compounds, and an outer layer including at least one alumina layer containing so much γ -type alumina that an X-ray intensity ratio of two specific crystal faces in X-ray diffraction is not smaller than 2, has better wear resistance and chipping resistance than the conventional cutting tools coated with a composite hard layer including the conventional alumina layer.

The invention was developed on the basis of these research results and is directed to:
 a cutting tool comprising a substrate whose surface is coated with a composite hard layer including an inner layer having one or more layers of titanium carbide, titanium nitride, titanium carbonitride, titanium carboxide, and titanium oxycarbonitride, and an outer layer having at least one alumina layer, wherein the inner layer contains so much α -type alumina that an X-ray intensity ratio I_A/I_B of two specific crystal faces A and B in X-ray diffraction is not smaller than 2, where the A-face and B-face denote faces of α -type alumina defined as those whose interfacial distances are 2.79 Å and 2.57 Å in ASTM4-0878, and I_A and I_B denote X-ray intensities of the faces A and B in X-ray diffraction.

5 The reason why the cutting tool according to the invention has better wear resistance and better chipping resistance compared with the conventional tools is thought to be that abnormal damage caused by friction between steel chips and the tool is unlikely to occur because α -type alumina, demonstrating orientation to the face A, makes the surface of the coated layer smooth.

10 Thus, when the alumina layer contains so much special α -type alumina that the ratio of X-ray intensity I_A of the face A to that I_B of the face B in X-ray diffraction is not smaller than 2, i.e., $I_A/I_B \geq 2$, wear 15 resistance and chipping resistance are further improved. Thus, the cutting tool whose surface is coated with the composite hard layer including this alumina layer has a longer lifetime even under severe working conditions such as high speed cutting.

15 Besides special α -type crystals whose X-ray intensity ratio (I_A/I_B) is not smaller than 2, the alumina layer according to the invention may contain alumina having a different crystallo-graphic structure. However, it is desirable that the amount of special α -type crystals in the alumina layer be at least not less than 30 %, preferably not less than 50 %, and most preferably not less than 70 %. The percentage of special α -type crystals is obtained from the following equation:

25 Percentage of special α -type crystals =

$$\frac{\text{sum of counts of all the peaks of } \alpha\text{-Al}_2\text{O}_3 \text{ in X-ray diffraction}}{\text{sum of counts of all the peaks of Al}_2\text{O}_3 \text{ in X-ray diffraction}} \times 100$$

30 It is not necessary for the alumina layer to be an outer-most layer. At least one layer of titanium compound may be formed on the alumina layer.

A method for forming the inventive alumina layer containing special α -type crystals whose peak intensity ratio (I_A/I_B) is not smaller than 2 is as follows.

35 During an alumina coating reaction, a substrate coated with titanium compounds is held in a mixed gas containing no CO₂ gas, but AlCl₃, H₂ and, if necessary, HCl for a predetermined time in the first step, and 40 is subsequently caused to react in a mixed gas containing CO₂, AlCl₃, H₂ and, if necessary, HCl in the second step.

It will be appreciated that the mixed gas used for the coating reaction may further contain H₂S if necessary.

45 The conditions for the alumina coating reaction are described in detail below:

First Step -

Temp. : 800 to 1050 °C , Time : 1 to 120 min.

Gas Composition : 0.5 to 20 vol % of AlCl₃, 0 to 20 vol % of HCl, remainder H₂

50

Second Step -

Temp. : 800 to 1050 °C

Gas Composition : 0.5 to 30 vol % of CO₂, 0.5 to 20 vol % of AlCl₃, 0 to 20 vol % of HCl, remainder H₂

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If necessary, 0.01 to 5 vol % of H₂S may be added at the beginning or in the middle of the second step. The composition of the mixed gas may be changed continuously during the transition from the first step to the second step.

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[Example]

The surface coated cutting tool according to the invention will be described in more detail by way of an example.

5 A mixed powder having the composition: 87%WC-2%TiC-1%TiN-4%TaC-6%Co was prepared according to a normal method. The mixed powder prepared in this way was compressed into a green compact, which was then sintered at a temperature of 1410° in vacuum for 1 hour. In this way, a cemented carbide substrate A of the form of ISO SNMG120408 was prepared.

10 Similarly, a mixed powder having the composition: 82%WC-5%TiC-5%TaC-8%Co was prepared according to a normal method. The mixed powder prepared in this way was compressed into a green compact, which was then sintered at a temperature of 1380° in vacuum for 1 hour. In this way, a cemented carbide substrate B of the form of ISO SNMG120408 was prepared.

15 On the surface of the cemented carbide substrate A, there was a tough surface layer of a thickness of 20 µm including substantially no hard disperse phase (Ti, Ta, W) (C, N) and having a Co-amount increased to a maximum of 1.8 times greater than the internal Co-amount. On the other hand, there was almost no difference in structure between the surface and internal portions of the cemented carbide substrate B.

20 Honing of as large as 0.05R (R is the radius of the edge of the cutting tool in mm) was applied to the cutting edges of the thus obtained cemented carbide substrates A and B, and the surfaces of the substrates were washed. The inventive surface coated cutting tools 1 to 8 were manufactured by coating the surface of substrate A under the conditions specified in TABLE-1 to TABLE-7 and by coating the surface of the substrate B under the conditions specified in TABLE-8. For the purpose of comparison, the conventional surface coated cutting tools 1 to 8 were manufactured by coating the surface of the substrate A under the conditions specified in TABLE-9 to TABLE-15 and by coating the surface of the substrate B under the conditions specified in TABLE-16.

25 X-ray diffraction was conducted for the inventive cutting tools 1 to 8 and the conventional cutting tools 1 to 8 to measure the X-ray intensity ratio I_A/I_B . The measurement results are shown in TABLE-17.

Further, a continuous cutting test and an interrupted cutting test were conducted for the above cutting tools under the following conditions. A wear width on the flank face was measured in the former test, whereas the lapse of time until chipping was measured in the latter test. The measurement results in the respective tests are again shown in TABLE-17.

[Cutting Test Conditions]

35

- Continuous Cutting -	
Work piece	JIS SCM440 (hardness : H _B 220) round bar
Cutting speed	250 m/min.
Feed rate	0.3 mm/rev.
Cutting depth	1.5 mm
Cutting time	20 min.
Coolant	none

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- Interrupted Cutting -	
Work piece JIS	SNCM439 (hardness : H _B 280) rectangular bar
Cutting speed	100 m/min.
Feed rate	0.236 mm/rev.
Cutting depth	3.0 mm
Cutting time	30 min.
Coolant	none

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TABLE-18, the ASTM table, defines faces by means of face index [indicated in (h, k, l)], but the specific faces of this $x\text{-Al}_2\text{O}_3$ are not yet identified. "Face A" and "face B" have been written in a blank column of this table in order to identify the faces. Fig. 1 is a graph showing X-ray diffraction data of the coating layer of the inventive cutting tool 5 in the example. I_A and I_B represent x-ray intensities of the faces A and B. A

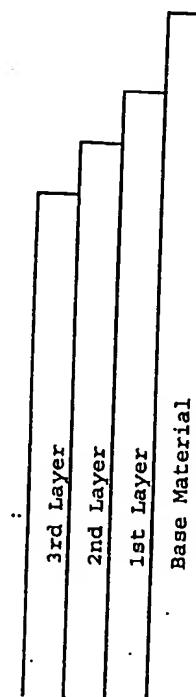
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theoretical d-value of the face A is 2.79 according to TABLE-18, but a measured d-value thereof is 2.812 which varies slightly from the theoretical d-value. The theoretical and measured d-values of the face B are 2.57 and 2.576, respectively. The horizontal axis of Fig. 1 represents 2θ which is an angle (in degree) an X-ray makes in the X-ray diffraction. Numerical values (2.812, 2.576, etc.) written on the respective peaks in this graph denote an interfacial distance d (in Å).

TABLE-1

LAYER	TYPE OF LAYER	THICK- NESS (μ m)	REAC. TEMP. (°C)	PRES- SURE (Torr)	TIME (MIN)	REACTION GAS COMPOSITION (VOL %)					
						TiCl ₄	CH ₄	CH ₃ CN	N ₂	CO	AlCl ₃
1st	TiN	0.2	910	50	2				25		
2nd	TiCN	9.0	910	50	2		0.6		25		
3rd	TiCNO	0.5	1010	50	2	1					
		2.0	1010	50	10				23	1	
4th	Al ₂ O ₃	2.0	1010	50	10					3	
		2.0	1010	50	120					2	4

(REM. denotes remainder)



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TABLE-2

LAYER	TYPE OF LAYER	THICKNESS (μm)	REAC. TEMP. ($^{\circ}\text{C}$)	PRESSURE (Torr)	TIME (MIN)	REACTION GAS COMPOSITION (VOL %)							CONDITIONS	
						TiCl ₄	CH ₄	CH ₂ CN	N ₂	CO	AlCl ₃	CO ₂	H ₂ S	H ₂
1st	TiN	0.2	900	50	2				25					REM.
2nd	TiCN	9.0	900	50	2	0.6	25							REM.
3rd	TiCNO	0.5	1010	50	2	1			15	1				REM.
4th	Al ₂ O ₃	2.0	1010	50	10					6				REM.
		2.0	1010	50	10						5	4		REM.
		2.0	1010	50	120						3	4	0.3	REM.
5th	TiN	0.5	900	300	1				70					REM.

(REM. denotes remainder)

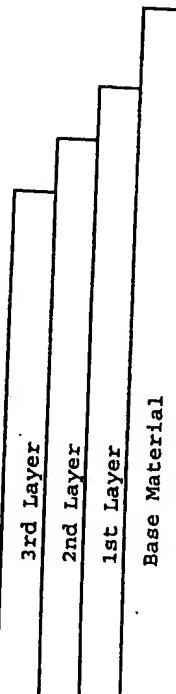


TABLE - 3

(REM. denotes remainder)

Base Material
3rd Layer
2nd Layer
1st Layer

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TABLE I-5

LAYER	TYPE OF LAYER	REACTION				CONDITIONS								
		THICK- NESS (μ m)	REAC. TEMP. ($^{\circ}$ C)	PRES- SURE (Torr)	TIME (MIN)	REACTION GAS COMPOSITION (VOL %)								
	TiCN					TiCl ₄	CH ₄	CH ₃ CN	N ₂	CO	AlCl ₃	CO ₂	H ₂ S	H ₂
1st	TiCN	6.0	870	50		2	0.8	32					REM.	
2nd	Al ₂ O ₃	6.0	990	50	20					5			REM.	
		6.0	990	50	30					2	4		REM.	
		6.0	990	50	300					2	7	0.5	REM.	2nd STEP

(REM. denotes remainder)

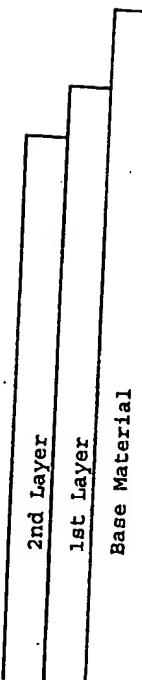


TABLE-6

LAYER	TYPE OF LAYER	THICK- NESS (μ m)	REAC. TEMP. ($^{\circ}$ C)	PRESS- URE (Torr)	TIME (MIN)	REACTION CONDITIONS						
						TiCl ₄	CH ₄	CH ₃ CN	N ₂	CO	AlCl ₃	CO ₂
1st	TiC	3.0	1020	50		3	9					
2nd	TiCN	3.0	1000	50		3	7		26			
		6.0	960	50	30							
3rd	Al ₂ O ₃	6.0	960	50	30					1		
		6.0	960	50	300					2	10	
										3	10	0.2
												REM.

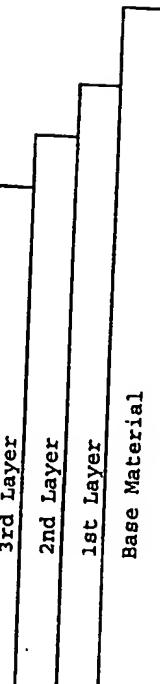
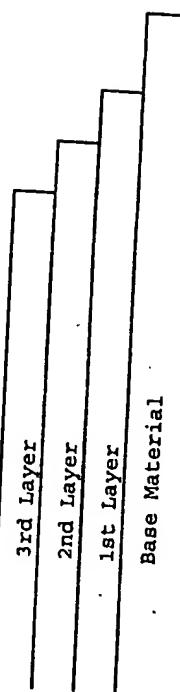
1st STEP
(REM. denotes remainder)

TABLE - 7

REACTION
CONDITIONS

LAYER	TYPE OF LAYER	THICK- NESS (μm)	REAC. TEMP. ($^{\circ}\text{C}$)	PRES- SURE (Torr)	TIME (MIN.)	REACTION GAS COMPOSITION (VOL %)						
						TiCl ₄	CH ₄	CH ₃ CN	N ₂	CO	AlCl ₃	CO ₂
1st	TiC	3.0	1020	50	3	9						
2nd	TiCN	3.0	1000	50	3	7	26					
		6.0	960	50	30							
3rd	Al ₂ O ₃	6.0	950	50	30					3		
		6.0	950	50	300					3	10	
4th	TiN	0.5	900	300	1					6	10	0.1
										55		
												REM.

(REM. denotes remainder)



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TABLE - 8

LAYER	TYPE OF LAYER	THICKNESS (μm)	REAC. TEMP. ($^{\circ}\text{C}$)	PRESSURE (Torr)	TIME (MIN)	REACTION CONDITIONS						
						TiCl ₄	CH ₄	CH ₃ CN	N ₂	CO	AlCl ₃	CO ₂
1st	TiCN	5.0	1020	50	3	7		26				
												REM.
2nd	Al ₂ O ₃	6.0	930	50	20					6		REM.
		6.0	930	50	360					6	2	0.05 REM.
												2nd STEP
												1st STEP
												2nd STEP

(REM. denotes remainder)

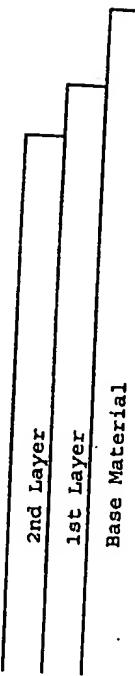


TABLE 9
REACTION
CONDITIONS

LAYER	TYPE OF LAYER	THICK- NESS (μm)	REAC. TEMP. ($^{\circ}\text{C}$)	PRES- SURE (TORR)	TIME (MIN)	REACTION GAS COMPOSITION (VOL %)					
						TiCl ₄	CH ₄	CH ₃ CN	N ₂	CO	AlCl ₃
1st	TiN	0.2	910	50	2				35		
2nd	TiCN	9.0	910	50	2				0.6	25	REM.
3rd	TiCN _O	0.5	1010	50	2	1			23	1	REM.
4th	Al ₂ O ₃	2.0	1020	50	120					6	4
:	:	:								0.3	REM.

(REM. denotes remainder)

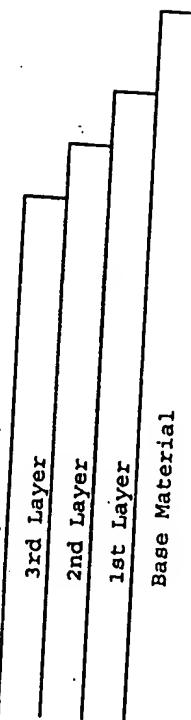


TABLE-10

LAYER	TYPE OF LAYER	THICKNESS (μm)	REAC. TEMP. ($^{\circ}\text{C}$)	PRES-SURE (Torr)	TIME (MIN)	REACTION GAS COMPOSITION (VOL %)						CONDITIONS
						TiCl ₄	CH ₄	CH ₃ CN	N ₂	CO	AlCl ₃	
1st	TiN	0.2	900	50		2			25			REM.
2nd	TiCN	9.0	900	50		2			0.6	20		REM.
3rd	TiCNO	0.5	1010	50		2			23	1		REM.
4th	Al ₂ O ₃	2.0	1020	50	120						2	4
5th	TiN	0.5	900	300		1			55		0.3	REM.
												REM.

(REM. denotes remainder)

3rd Layer 2nd Layer 1st Layer

(REM. denotes remainder)

TABLE-11

(REM. denotes remainder)

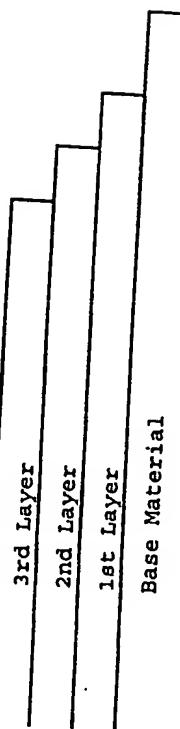


TABLE-12

LAYER	TYPE OF LAYER	REACTION CONDITIONS				REACTION GAS COMPOSITION (VOL %)								
		THICKNESS (μm)	REAC. TEMP. ($^{\circ}\text{C}$)	PRES-SURE (TORR)	TIME (MIN)	TiCl ₄	CH ₄	CH ₃ CN	N ₂	CO	AlCl ₃	CO ₂	H ₂ S	H ₂
1st	TiN	0.5	920	120		3				57				
2nd	TiCN	6.0	920	50		2			0.8	32				REM.
3rd	TiCNO	0.5	1000	100		3	1			25	1			REM.
4th	Al ₂ O ₃	6.0	1000	50										REM.
5th	TiN	0.5	900	300		1						3	10	0.2 REM.
												55		REM.

(REM. denotes remainder)

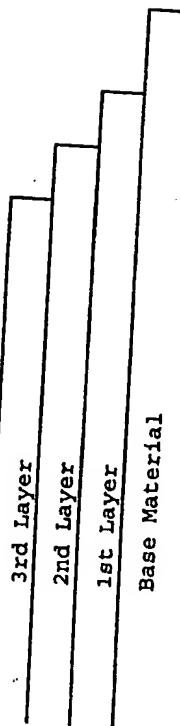


TABLE-13

LAYER	TYPE OF LAYER	THICK- NESS (μm)	REAC. TEMP. ($^{\circ}\text{C}$)	PRES- SURE (Torr)	TIME (MIN)	REACTION CONDITIONS						
						TiCl ₄	CH ₄	CH ₃ CN	N ₂	CO	AlCl ₃	CO ₂
1st	TiCN	6.0	870	50		2		0.8	32			
2nd	Al ₂ O ₃	6.0	1020	50	300					1	7	0.5

(REM. denotes remainder)

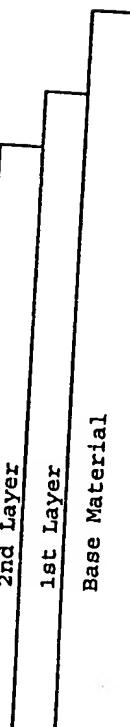


TABLE 14

LAYER	TYPE OF LAYER	THICK- NESS (μm)	REAC. TEMP. ($^{\circ}\text{C}$)	PRES- SURE (Torr)	TIME (MIN)	REACTION CONDITIONS						REACTION GAS COMPOSITION (VOL %)				
						TiCl ₄	CH ₄	CH ₃ CN	N ₂	CO	AlCl ₃	CO ₂	H ₂ S	H ₂	REM.	
1st	TiC	3.0	1020	50		3	9								REM.	
2nd	TiCN	3.0	1000	50		3	7								REM.	
3rd	Al ₂ O ₃	6.0	1000	50	300								3	10	0.2	REM.

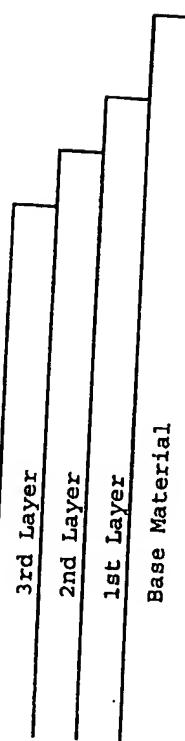
(REM. denotes remainder)

3rd Layer 2nd Layer 1st Layer Base Mater

TABLE-15

LAYER	TYPE OF LAYER	THICK- NESS (μm)	REAC. TEMP. ($^{\circ}\text{C}$)	PRES- SURE (Torr)	TIME (MIN)	REACTION CONDITIONS						
						TiCl ₄	CH ₄	CH ₂ CN	N ₂	CO	AlCl ₃	CO ₂
1st	TiC	3.0	1020	50		3	9					
2nd	TiCN	3.0	1000	50		3	7					
3rd	Al ₂ O ₃	6.0	990	50	300				26			
4th	TiN	0.5	900	300		1				8	10	0.6
										55		REM.
												REM.

(REM. denotes remainder)



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TABLE-16

LAYER	TYPE OF LAYER	THICK- NESS (μ m)	REAC. TEMP. (°C)	PRES- SURE (Torr)	TIME (MIN)	REACTION CONDITIONS				
						TiCl ₄	CH ₄	CH ₃ CN	N ₂	CO
1st	TiCN	5.0	1020	50		3	7		26	
2nd	Al ₂ O ₃	6.0	1000	50	300					6

(REM. denotes remainder)

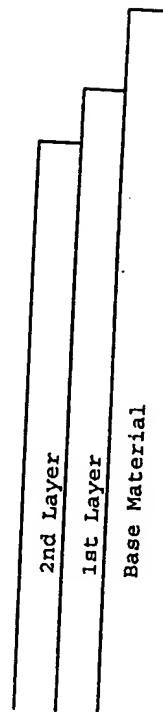


TABLE-17

CATEGORY	I_A/I_B	RATIO (%) WHERE $I_A/I_B \geq 2$	FLANK WEAR WIDTH (mm) AFTER 20 MIN. CONTINUOUS CUTTING TEST		LAPSE OF TIME UNTIL CHIPPING IN INTERRU- PTED CUTTING TEST (MIN.)
			95	0.21	
PRESENT	1	8	95	0.21	10.1
	2	7	95	0.20	8.3
	3	30	100	0.18	8.9
	4	25	100	0.20	8.8
INVENTION	5	12	100	0.24	7.2
	6	6	90	0.27	7.9
	7	5	90	0.26	8.5
	8	2	100	0.31	7.0
PRIOR	1	0.7	*	0	0.44
	2	0.7	0	0.43	5.3
	3	0.9	0	0.51	5.5
	4	0.9	0	0.51	5.0
ART	5	0.2	0	0.54	5.1
	6	0.6	0	0.49	4.0
	7	0.5	0	0.53	5.2
	8	0.7	0	0.50	5.8

* This ratio is set to 0 since the conventional surface coated cutting tools contain no special κ -type Al_2O_3 of $I_A/I_B \geq 2$, though containing normal κ -type Al_2O_3 of $I_A/I_B < 2$.

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ASTM 4-0878

				TABLE-18				KAPPA ALUMINUM OXIDE				$\kappa\text{-Al}_2\text{O}_3$				KAPPA ALUMINA			
d	1.39	2.57	2.11	6.2					d	1/I₁	hk1	d	1/I₁	hk1	d	1/I₁	hk1		
Rad. CuK α	λ 1.5405	Filler	Yes						6.2	30		1.49	30						
Dia. 144mm	Cut off	Coll.							4.5	20		1.45	30						
I/I ₁	100	80	80	30	d corr.abs.?				4.2	10		1.43	80						
Ref. STUMPF ET AL., IND. END. CHEM. 42 1398-1403 (1950)						3.04			3.04	40		1.39	100						
Sys.						2.79			2.79	60	Face A	1.34	30						
a ₀	b ₀	c ₀	s.g.			2.70			2.70	20	Face B	2.57	80						
α	β	λ	A			2.57			2.57	80		2.41	30						
Ref.			Z			2.41			2.41	30		2.32	40						
8a	n $\omega\beta$	$\epsilon\gamma$	sign			2.32			2.32	40		2.26	10						
2v	D	mp	Color			2.26			2.26	10		2.16	10						
Ref.						2.16			2.16	10		2.11	80						
ALPHA ALUMINA TRIHYDRATE HEATED 1 HOUR AT 1000°C IN ROOM AIR.						2.06			2.06	30		1.87	60						
D- AND I-VALUES REVISED BY STUMPF IN 1950, USING CORUNDUM AS STANDARD.						1.99			1.99	40		1.82	30						

Faces A and B are faces specified in ASTM as follows: Face A : d = 2.79 \AA , Face B : d = 2.57 \AA . d-values of the faces A and B may vary due to a lattice defect, but even the faces defined by those varied values may be assumed to be faces A and B.

55 [Effect of the invention]

As is clear from the results shown in TABLE-17, the value of I_A/I_B of x-type alumina of any of the inventive cutting tools 1 to 8 is not smaller than 2. On the contrary, the value of I_A/I_B of x-type alumina of

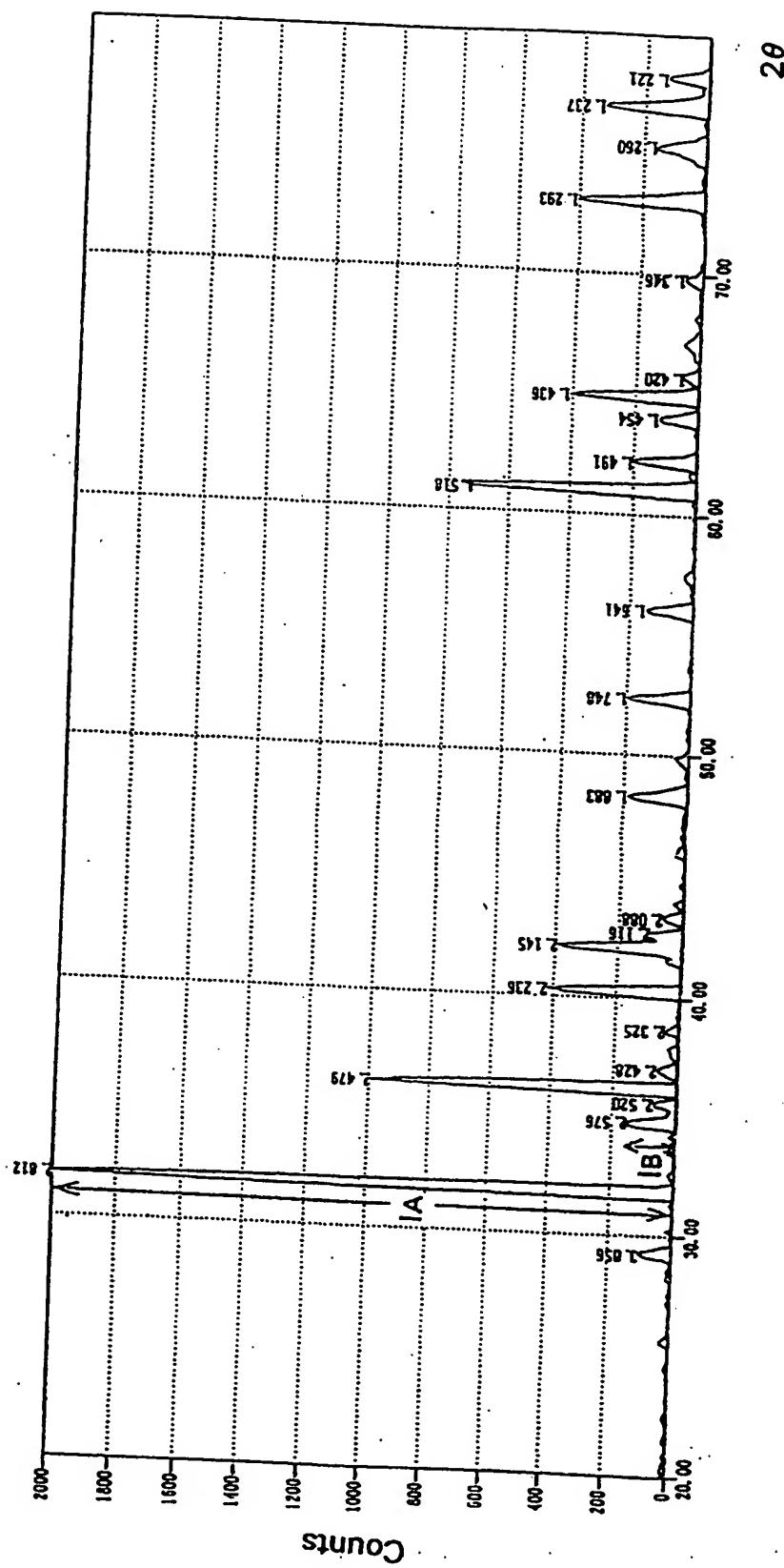
any of the conventional cutting tools 1 to 8 is smaller than 2. Further, any of the inventive cutting tools 1 to 8 demonstrates a smaller wear width on the flank face in the continuous cutting test and has a longer lapse of time until chipping in the interrupted cutting test, compared with the conventional cutting tools 1 to 8.

Thus, the surface coated cutting tool according to the invention has a better performance than the conventional tools, and the use thereof leads to a reduced frequency of replacement, thereby contributing greatly to development of industries.

Claims

10. 1. A cutting tool comprising a substrate whose surface is coated with a composite hard layer including an inner layer having one or more layers of titanium carbide, titanium nitride, titanium carbonitride, titanium carboxide, and titanium oxycarbonitride, and an outer layer having at least one alumina layer,
wherein the alumina layer contains so much *x*-type alumina that an X-ray intensity ratio I_A/I_B of two specific crystal faces A and B in X-ray diffraction is not smaller than 2, where the faces A and B denote faces of *x*-type alumina defined as those whose interfacial distances are 2.79Å and 2.57Å in ASTM4-0878, and I_A and I_B denote X-ray intensities of the faces A and B in X-ray diffraction.
15. 2. A cutting tool according to claim 1, wherein the alumina layer contains at least 30 % of *x*-type alumina.
20. 3. A cutting tool according to claim 2, wherein the alumina layer contains at least 50 % of *x*-type alumina.
25. 4. A cutting tool according to claim 3, wherein the alumina layer contains at least 70 % of *x*-type alumina.
30. 5. A cutting tool according to claim 1, wherein the alumina layer containing *x*-type alumina is the uppermost layer.
35. 6. A process for producing a cutting tool according to claim 1 by coating the surface of a substrate with a composite hard layer including an inner layer having one or more layers of titanium carbide, titanium nitride, titanium carbonitride, titanium carboxide, and titanium oxycarbonitride and an outer layer having at least one alumina layer, wherein the substrate coated with titanium compounds is held in a mixed gas containing no CO₂ gas but AlCl₃, H₂ and, if necessary, HCl for a predetermined time in the first step and is subsequently caused to react in a mixed gas containing CO₂, AlCl₃, H₂ and, if necessary, HCl in the second step so that an alumina layer containing so much *x*-type alumina, that an X-ray produced, where the faces A and B denote faces of *x*-type alumina defined as those whose interfacial distances are 2.79Å and 2.57Å in ASTM4-0878 and I_A and I_B denote X-ray intensities of the faces A and B in X-ray diffraction.
40. 7. A process according to claim 6 characterized in that the mixed gas used for the coating reaction further contains H₂S.
45. 8. A process according to claim 6 characterized in that the conditions for the alumina coating reactions in the first step are a temperature of 800 to 1050 °C, a time of 1 to 120 minutes, a gas composition of 0.5 to 20 vol % of AlCl₃, 0 to 20 vol % of HCl, remainder H₂ and in the second step a temperature of 800 to 1050 °C and gas composition of 0.5 to 30 vol % of CO₂, 0.5 to 20 vol % of AlCl₃, 0 to 20 vol % of HCl, remainder H₂.
50. 9. A process according to claim 8 wherein 0.01 to 5 vol % of H₂S have been added at the beginning or in the middle of the second step.
55. 10. A process according to claim 8 wherein the composition of the mixed gas is changed continuously during the transition from the first step to the second step.

Fig. 1



2θ



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EUROPEAN SEARCH REPORT

Application Number
EP 94 10 8885

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int.Cl.6)		
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim			
X	THIN SOLID FILMS, 15 JULY 1992, SWITZERLAND, VOL. 214, NR. 2, PAGE(S) 132 - 143, ISSN 0040-6090 Vuorinen S et al 'Phase transformation in chemically vapour-deposited kappa -alumina' * page 134, right column, line 5 - line 11; table 4 *	1-5	C23C16/02 C23C30/00		
X	EP-A-0 408 535 (SECO TOOLS AB) 16 January 1991 * column 5, line 6 - line 15 *	1-5			
X	EP-A-0 120 632 (GEN ELECTRIC) 3 October 1984 * example 1 *	6,8			
X	EP-A-0 083 842 (GEN ELECTRIC) 20 July 1983 * example 1 *	6,8			
A,D	EP-A-0 045 291 (SANDVIK AB) 3 February 1982 * example 1 *	7,9	TECHNICAL FIELDS SEARCHED (Int.Cl.6)		
A	DE-A-36 33 986 (SCHMALKALDEN WERKZEUG) 25 June 1987 * claims 9,14 *	10	C23C		
A	PATENT ABSTRACTS OF JAPAN vol. 013, no. 466 (C-646) 20 October 1989 & JP-A-01 180 980 (DAIJIETSUTO KOGYO KK) 18 July 1989 * abstract *	1-10			
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The present search report has been drawn up for all claims					
Place of search	Date of compilation of the search	Examiner			
THE HAGUE	7 November 1994	Ekhult, H			
CATEGORY OF CITED DOCUMENTS					
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document					
T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document					



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DOCUMENTS CONSIDERED TO BE RELEVANT									
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.)						
E	<p>DATABASE WPI</p> <p>Section Ch, Week 9432, Derwent Publications Ltd., London, GB; Class L02, AN 94-259893 & JP-A-6 190 605 (MITSUBISHI MATERIALS CORP) 12 July 1994 * abstract *</p> <p>-----</p>	1							
TECHNICAL FIELDS SEARCHED (Int.Cl.)									
<p>The present search report has been drawn up for all claims</p> <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 33%;">Place of search</td> <td style="width: 33%;">Date of completion of the search</td> <td style="width: 33%;">Examiner</td> </tr> <tr> <td>THE HAGUE</td> <td>7 November 1994</td> <td>Ekhult, H</td> </tr> </table>				Place of search	Date of completion of the search	Examiner	THE HAGUE	7 November 1994	Ekhult, H
Place of search	Date of completion of the search	Examiner							
THE HAGUE	7 November 1994	Ekhult, H							
CATEGORY OF CITED DOCUMENTS <ul style="list-style-type: none"> X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document 									
<ul style="list-style-type: none"> T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document 									